Gas induced reduction synthesis of Sb$_2$Te$_3$ and Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanosheets and their evolvement mechanism

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Abstract

Binary Sb$_2$Te$_3$ and ternary Bi$_{0.5}$Sb$_{1.5}$Te$_3$ hexagonal nanosheets were synthesized by a gas-induced reduction (GIR) method, with Sb$_2$(OCH$_2$CH$_2$O)$_3$, TeO$_2$ and Bi(NO$_3$)$_3$·5H$_2$O as raw materials and hydrazine hydrate as a reducing agent. Structure and composition analyses reveal that the samples are of pure phase with corresponding atomic ratios. Electron microscopy analyses indicate that the as-prepared products are uniform and highly crystallized. The formation process was studied in detail by observing temperature-dependent and time-dependent products. It is found that the selective adsorption mechanism may be responsible for the growth of the hexagonal nanosheets. The GIR route is a simple and flexible route to the Bi—Sb—Te alloys and can be easily extended to the synthesis of other low-dimensional chalcogenide nanostructures.

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1. Introduction

Antimony telluride (Sb$_2$Te$_3$)-based compounds are very promising materials for thermoelectric (TE) applications in solid-state refrigeration and power generation [1–4]. The conversion efficiency of a TE material is evaluated by the dimensionless figure-of-merit $ZT(=\sigma^2T/\kappa)$, where $T$ is the absolute temperature, $\sigma$ is the electrical conductivity, $\kappa$ is the Seebeck coefficient, and $\kappa$ is the thermal conductivity of the material. If the $ZT$ value of TE materials can reach 3, TE coolers and TE power generators will become highly competitive with conventional compressor-based refrigerators or even surpass them [5].

Both theoretical and experimental works have indicated that “nanostructuring” of the TE materials is a primarily promising strategy for enhancing $ZT$, due to both a higher density of states and an increased phonon scattering hence reduced lattice thermal conductivity in nanomaterials [6–12]. For example, Bi$_2$Te$_3$/Sb$_2$Te$_3$ superlattices were reported to have a $ZT$ value of ~2.4 at room temperature [12]. Thus, more and more attentions have recently been paid to the synthesis of Sb$_2$Te$_3$ nanomaterials. Several methods, such as the solvothermal/hydrothermal process, decomposition of a single-source precursor, electrochemical deposition into porous anodic aluminum oxide film, electrochemical atomic layer epitaxy, microwave assisted synthesis, and microwave-stimulated, surfactant-directed, wet-chemical approach, have been successfully employed for the fabrication of Sb$_2$Te$_3$ nanostructures [13–24].

Since Sb$_2$Te$_3$ has the same crystal structure as Bi$_2$Te$_3$, and Sb$_2$Te$_3$ nanosheet grown along the basal plane of the crystal
structure possesses better TE properties than that grown along other directions [2,25], it is desirable to explore methods to synthesize uniform Sb$_2$Te$_3$ nanosheets. Zhou et al. [13] and Zhang et al. [18] synthesized Sb$_2$Te$_3$ nanosheets via microwave-assisted synthesis and hydrothermal methods. However, these methods are difficult to prepare pure ternary (such as Bi$_{0.5}$Sb$_{1.5}$Te$_3$) nanoparticles without using an organic surfactant or complexing agent [26,27]. In the present study, we synthesized Sb$_2$Te$_3$ and Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanosheets using a new gas induced reduction (GIC) method, by which we recently have successfully synthesized single crystalline Sb$_2$Se$_3$ nanowires/nanobelts [28] and Sb$_2$Se$_3$ films consisting of Sb$_2$Se$_3$ nanowires [29]. The formation process of the Sb$_2$Te$_3$ nanosheets are studied in detail here and the formation mechanism of the Sb$_2$Te$_3$ nanosheets are also explored.

2. Experimental section

In a typical run, glass slides (20 \times 20 \text{ mm}^2) cleaned with CC$_4$, ethanol, acetone, and distilled water and then dried in air were used as substrates. The precursor solution for the synthesis of Sb$_2$Te$_3$ nanostructures was prepared as follows: 0.5 mmol of Sb$_2$(OCH$_2$CH$_2$O)$_3$ [Sinopharm Chemical Reagent Co.; analytical reagent (AR)], 1.5 mmol of TeO$_2$ (Sinopharm Chemical Reagent Co.; AR), 0.4 mL of nitric acid, and 60 mL of ethylene glycol (EG) (Shanghai Meixing Chemical Co.; AR) were sequentially added to a 100-mL beaker; while the precursor solution for the synthesis of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanostructures was prepared as follows: 0.3 mmol of Bi(NO$_3$)$_3$5H$_2$O, 0.45 mmol of Sb$_2$(OCH$_2$CH$_2$O)$_3$ (Sinopharm Chemical Reagent Co.; AR), 1.8 mmol of TeO$_2$ (Sinopharm Chemical Reagent Co.; AR), 0.4 mL of nitric acid, and 60 mL of ethylene glycol (EG) were sequentially added to a 100-mL beaker. These mixtures were heated to 95 °C with stirring until they became transparent.

The glass slides were placed on a Teflon cylinder in Teflon-lined autoclave. Five droplets of the precursor solution were dropped onto the glass slides, and 1 mL of 85 vol % hydrazine hydrate was injected into the bottom of the Teflon container. The autoclave was sealed, heated to a selected temperature in the range of 160–250 °C at a heating rate of 3 °C/min, held at that temperature for 2 h, and then naturally cooled to room temperature. Products grown on the glass slides were collected and directly characterized.

The products were examined by powder X-ray diffraction (XRD, Bruker D8 Advance) with Cu Kα radiation (λ = 1.5406 Å). The morphology, structure, and composition of the products were examined by field-emission scanning electron microscopy (FESEM, Quanta 200 FEG) accompanied by energy dispersive X-ray spectroscopy (EDS, Oxford 7582), transmission electron microscopy (TEM, Hitachi H-800), and high-resolution TEM (HRTEM, Philips TECNAI-20), respectively.

3. Results and discussion

3.1. The effect of reaction temperature on the synthesized product

XRD patterns of the products obtained from various reaction temperatures are shown in Fig. 1. The XRD patterns of the products synthesized at 160, 190, 220 and 250 °C, as shown in Fig. 1a–d, can be indexed to hexagonal Te element (JCPDS card 36-1452) and orthorhombic Sb$_2$O$_3$ (JCPDS card 11-689), Te and cubic Sb$_2$O$_3$ (JCPDS card 5-534), cubic Sb$_2$O$_3$ and Sb$_2$Te$_3$, and rhombohedral Sb$_2$Te$_3$ (JCPDS card 71-0393), respectively. As the reaction temperature increases from 160 to 190 °C, the orthorhombic Sb$_2$O$_3$ transforms to cubic Sb$_2$O$_3$. As the temperature increases from 190 to 220 °C, the peak intensity of cubic Sb$_2$O$_3$ decreases while the peaks for the target product Sb$_2$Te$_3$ appear. That the diffraction peaks are very sharp in Fig. 1d, indicating that the Sb$_2$Te$_3$ product is in good crystallinity. This suggests that heating at 250 °C for 120 min is a proper reaction condition for the synthesis of Sb$_2$Te$_3$.

Fig. 2a–f show the FESEM images of the samples obtained at 160, 190, 220 and 250 °C for 120 min. The sample synthesized at 160 °C mainly consists of nanorods (~150–350 nm in diameter and 1–5 μm in length) with sharp ends (Fig. 2a). These nanorods may be Te nanorods from the XRD results (Fig. 1a) and our previous experiment (see supporting information SFig. 1), though it is hard to precisely identify the Sb$_2$O$_3$ entity in Fig. 2a. The product obtained at 190 °C is assumed to be cubic Sb$_2$O$_3$, with size of 1–2 μm, accompanied with numerous flocculent nanofibers (Fig. 2b). Irregular flakes (Fig. 2c), which look like knitted fabrics at a high magnification (Fig. 2d), were obtained when the synthesis temperature increased to 220 °C. The knitted fabrics could be considered as the rudiments of the final product- Sb$_2$Te$_3$ nanosheets (see hereinafter), which presents the phase
transformation from Te and Sb$_2$O$_3$ into Sb$_2$Te$_3$ with (009) plane orientation. When the synthesis temperature was 250°C, hexagonal nanosheets with edge length of 600–1200 nm and thickness of 30–50 nm (Fig. 2e–f) were obtained. EDS analysis indicates that the nanosheets are composed of Sb and Te. Quantitative EDS analysis (not shown in the paper) reveals that the atomic ratio of Sb:Te is very close to the nominal composition of Sb$_2$Te$_3$.

TEM observations further confirm that the products obtained at 250°C are hexagonal nanosheets. Fig. 3a shows a typical TEM image of the nanosheets synthesized at 250°C for 120 min. The hexagonally symmetric spots in the SAED pattern (Fig. 3b) indicate excellent single crystallinity.

As the product synthesized at 250°C for 120 min shows the best result (the product consisting of regular hexagonal Sb$_2$Te$_3$ nanosheets), the synthesis temperature of the subsequent experiments was fixed at 250°C. We varied other processing parameters (e.g., holding times) to investigate the possible formation mechanism of the nanosheets and the effect of synthesis conditions on the product.

3.2. The structure evolution of the products

In order to investigate the growth mechanism of the Sb$_2$Te$_3$ nanosheets, a series of experiments with different reaction times have been explored. The reaction system was heated to 250°C in an oven with a heating rate ~3 °C/min and then held for a selected time from 0 to 120 min.

XRD was performed and the resulting XRD patterns for the samples are shown in Fig. 4. XRD pattern of the sample heated to 250°C and held for 0 min (shown in Fig. 4a) reveals that the sample consists of orthorhombic Sb$_2$O$_3$ (JCPDS card 11-689), rhombohedral TeO$_3$ (JCPDS card 20-1240) and Te$_4$O$_9$ (JCPDS card 71-355), and hexagonal Te (JCPDS card 36-1452). In the XRD pattern for the sample held at 250°C for 20 min (Fig. 4b), TeO$_3$ peaks vanish and the peaks of Te$_4$O$_9$ shift from those presented in Fig. 4a to (003) and (300) planes. The diffraction peaks of Te have been enhanced significantly, while the orthorhombic Sb$_2$O$_3$ (JCPDS card 11-689) starts its crystal transformation from orthorhombic to cubic structure (JCPDS card 5-534). In the XRD pattern for the sample held for 40 min
(Fig. 4c), new peaks appear at ~26.14° and ~28.74°, which correspond to (110) and (111) planes of tetragonal TeO₂, respectively. For the sample held for 60 min (Fig. 4d), Te element and rhombohedral TeO₃ still exist, and the phase transformation of Sb₂O₃ is complete. Meanwhile, the tetragonal TeO₂ peak vanishes and an orthorhombic one (JCPDS card 5-534) appears instead. For the sample held for 80 min (Fig. 4e), the rhombohedral TeO₃ peak vanishes and the orthorhombic TeO₂ (JCPDS card 5-534) peak has been replaced by another orthorhombic TeO₂ (JCPDS card 9-433). Meanwhile, hexagonal Sb₂Te (JCPDS card 80-1722) is observed (at ~28.48° and ~39.07° relevant with (103) and (016) planes of Sb₂Te, respectively). Additionally, the (009) plane peak of hexagonal target product Sb₂Te₃ (JCPDS card 71-393) appears (at ~26.32°); in accordance with the result obtained from Fig. 1c. In the XRD pattern for the sample held for 100 min (Fig. 4f), all the peaks of the tellurium oxides vanish, the (009) plane peak of Sb₂Te₃ significantly decreases, whereas the peaks of hexagonal Sb₂Te have been significantly enhanced. At this stage, cubic Sb₂O₃ and hexagonal Te are still detectable with their overlapping peaks at ~27.58° and the (102) plane peak at ~29.2° for Te. In the sample held for 120 min, all the intermediate transition phases vanish and sharp XRD pattern of Sb₂Te₃ is observed (Fig. 4g).

In order to understand the phase evolvement process and explore the details of chemical mechanism involved, three additional experiments were performed as described below.

Experiment A was carried out at 250 °C for 120 min. The precursor used was only TeO₂ dissolved in EG without using any hydrazine hydrate. XRD analysis indicates that the product is hexagonal Te (JCPDS card 36-1452 and 85-559). This indicates that HTeO₂⁺ can be reduced to elemental Te by EG. In other experiments used hydrazine hydrate, it is found that the precursor solution has changed from acidic to basic before the temperature reached 250 °C by pH-test stripe, indicating that hydrazine hydrate dissolved into the precursor in the heating process from room temperature to 250 °C. The experimental results reveal that the formation of Te at the initial stage (Fig. 4a) can be derived from HTeO₂⁺ by EG and TeO₃²⁻ by hydrazine.

Experiment B was conducted at 250 °C for 120 min with the same heating and cooling rates, using hydrazine hydrate as a reductant. The precursor solution was prepared by only dissolving Sb₂(OCH₂CH₂O)₃ in EG, without addition of any TeO₂. XRD analysis reveals that the product is Sb₂O₃ (JCPDS card 5-534) rather than Sb (see supporting information SFig. 2). This indicates that HTeO₂⁺ can be reduced to elemental Te by EG. In other experiments used hydrazine hydrate, it is found that the precursor solution has changed from acidic to basic before the temperature reached 250 °C by pH-test stripe, indicating that hydrazine hydrate dissolved into the precursor in the heating process from room temperature to 250 °C. The experimental results reveal that the formation of Te at the initial stage (Fig. 4a) can be derived from HTeO₂⁺ by EG and TeO₃²⁻ by hydrazine.

We therefore propose that the formation of Sb₂Te₃ is related to the disproportionation reaction of Te in basic medium: the freshly reduced Te disproportions to Te²⁻, TeO₄²⁻ (Te⁶⁻) and TeO₃²⁻ (Te⁴⁻). In combination with the XRD results of the samples synthesized at 250 °C held for 0–60 min, the
diffraction peaks of Sb$_2$O$_3$ and the fact that Te can always be detected rather than any peaks for Sb$_2$Te$_3$, this implies that the formation of Sb$_2$Te$_3$ is not the direct result of the reaction between Te$^2^+$ and Sb$_2$O$_3$.

Experiment C was carried out under the same conditions as described in the second section, but with excess nitric acid added in the precursor solution. Only cubic Sb$_2$O$_3$ phase (JCPDS card, no. 5-534) was detected by XRD (see supporting information, SFig. 3). This indicates that the acidic media hinders the disproportionation reaction of Te, suggesting that the disproportionation reaction is a key step for the formation of Sb$_2$Te$_3$.

Based on the above experiments, the following reactions related to the formation mechanism of the Sb$_2$Te$_3$ are proposed:

\[
\text{TeO}_2 + H^+ \rightarrow \text{HTeO}_2^+ 
\]

(1)

\[
\text{Sb}_2(\text{OCH}_2\text{CH}_2\text{O})_3 + 3\text{H}^+ \rightarrow \text{Sb}_2\text{O}_3 + 3\text{CH}_2\text{CH}_2\text{OH}^+ 
\]

(2)

\[
2\text{HTeO}_2^+ + \text{C}_3\text{H}_6\text{O}_4(\text{EG}) \rightarrow 2\text{Te} + 2\text{H}_2\text{O} + 2\text{H}^+ + \text{C}_3\text{H}_6\text{O}_4 
\]

(3)

\[
\text{TeO}_3^{2-} + \text{N}_2\text{H}_4 \rightarrow \text{Te} + \text{N}_2 \uparrow + 2\text{OH}^- + \text{H}_2\text{O} 
\]

(4)

\[
4\text{Te} + 8\text{OH}^- \rightarrow 3\text{Te}^{2-} + \text{TeO}_4^{2-} + 4\text{H}_2\text{O} 
\]

(5)

\[
3\text{Te} + 6\text{OH}^- \rightarrow 2\text{Te}^{2-} + \text{TeO}_3^{2-} + 3\text{H}_2\text{O} 
\]

(6)

\[
\text{Sb}_2\text{O}_3 + \text{Te}^{2-} + \text{N}_2\text{H}_4 \rightarrow [\text{Sb}_x\text{Te}_y]^{n-} + \text{NH}_3 \uparrow + \text{N}_2 \uparrow + \text{H}_2\text{O} 
\]

(7)

\[
[Sb_x\text{Te}_y]^{n-} \rightarrow <009> \text{Sb}_2\text{Te}_3 + \text{Sb}_2\text{Te} 
\]

(8)

\[
\text{Sb}_2\text{Te} + \text{Te} \rightarrow \text{Sb}_2\text{Te}_3 
\]

(9)

Tellurium dioxide (TeO$_2$) dissolved into the acidic solution and formed HTeO$_2^+$ (Reaction 1) in the precursor solution, while Sb$_2$(OCH$_2$CH$_2$O)$_3$ was transformed into Sb$_2$O$_3$ (Reaction 2). The newly formed HTeO$_2^+$ was then reduced into Te by EG (Reaction 3) in the acidic medium at the initial heating stage. As the reaction temperature increased, hydrazine evaporated and dissolved into the solution (even before the reaction temperature reached 250 °C), resulting in the precursor solution changing from acidic to basic. Meanwhile, HTeO$_2^+$ in the acidic environment transformed into TeO$_3^{2-}$ in the basic one, which was reduced into Te (Reaction 4). Then the newly formed Te from Reactions 3 and 4 disproportionate into Te$^{2-}$, TeO$_4^{2-}$ (Reaction 5) and TeO$_3^{2-}$ (Reaction 6), evidenced by the appearance of TeO$_3$, Te$_4$O$_9$ and TeO$_2$ in different stages shown in Fig. 2a–e. The formed TeO$_4^{2-}$ or TeO$_3^{2-}$, were immediately reduced into Te by the dissolved N$_2$H$_4$ (Reaction 4), and the fresh Te disproportionate again according to Reactions 5 and 6.

As the cubic Sb$_2$O$_3$ peaks continued existing in the XRD patterns of the sample held for 80–100 min, the Sb$_2$O$_3$ combined with Te$^{2-}$ ions into oxygen-contained groups, followed by reduced into various [Sb$_x$Te$_y$]$^{n-}$ building blocks (Reaction 7), which self-assembled to variety of polyanions by the choice of ammonium cations as the structure-directing agents. That is, intermediate phases Sb$_2$Te and initial Sb$_2$Te$_3$ with (009) plane preferential orientation, formed when the reaction time was in the range of 80–100 min intervals, and finally pure Sb$_2$Te$_3$ phase formed (Reaction 8 and 9) as the reaction time was long enough (>120 min).

Fig. 5 shows typical FESEM images of the as-synthesized products heated at 250 °C and held for various reaction times. The sample held for 0 min. (Fig. 5a) consists of prototype of lamellar particles (2–3 μm in size) featured with rough surface and unclear interfaces. For the sample held for 20 min (Fig. 5b), the interfaces between these grains become clear. The samples held for 40 and 60 min (Fig. 5c–d) are composed of prototype of hexagonal grains with numerous nanoparticles absorbed on their surfaces. The absorbed nanoparticles aligned into triangles and hexagons, revealing a selective adsorption process in a liquid reaction environment, during which intermediate product molecules deposited onto the proper sites and formed these patterns. The samples held for 80 and 100 min (Fig. 5e–f) consist of lamellae with plane sizes of about 1–2 μm and smooth surfaces. The sample held for 120 min (Fig. 5g–h) is composed of hexagonal nanosheets with 1D nanowire array vertically aligned onto the nanosheet surface derived from the selective absorption.

For better observation and investigation of the selective adsorption mechanism occurred in the GIR process of Sb$_2$Te$_3$, nanosheet growth, a desolvation process was conducted on the precursor solution by heating the glass substrate at 200 °C for 30 min to get a slightly moist precursor film. Then the precursor film was undergone a relative long-term reduction process at 250 °C for 12 h, during which the product was gradually formed in a very slow gas-reducer diffusion and induction process.

As shown in Fig. 6, all XRD peaks of the product can be indexed to the reported rhombohedral Sb$_2$Te$_3$ (JCPDS card 71-0393) which shows a (001) preferred orientation. The bump from 20° to 40° in Fig. 6 indicates that the product mainly consists of crystallized rhombohedral Sb$_2$Te$_3$ and some non-crystalline substances.

Fig. 7 clearly shows the evolvement process of the proposed selective adsorption growth mechanism. Species spontaneously tended to form hexagonal frameworks initially according to the crystal structure conformity principle. The hollow hexagonal architecture further implemented in-plane assembly by absorbing nanoparticles or ion groups, and gradually fulfilled the hollow spaces into the solid hexagonal mosaics, and finally the small nanoparticles connected together into a smooth hexagonal. The scheme of the selective adsorption growth mechanism of the Sb$_2$Te$_3$ nanoplates is depicted in Fig. 8.

3.3. Structure characterization of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanosheets

To examine the generality of this synthesis route, ternary V–VI based alloy, Bi$_{0.5}$Sb$_{1.5}$Te$_3$ has been
synthesized by the same route. Fig. 9 shows the XRD pattern of the sample synthesized at 250 °C for 18 h. All the peaks can be indexed to the reported rhombohedral Bi$_{0.5}$Sb$_{1.5}$Te$_3$ (JCPDS card 49-1713), indicating that Bi$_{0.5}$Sb$_{1.5}$Te$_3$ has been successfully synthesized by the same route. The sharp peaks of the XRD pattern indicate the excellent crystallinity of the product. The product consists of hexagonal nanosheets with edge length ~1–2 μm and thickness tens of nanometers (in the FESEM and TEM images shown in Fig. 10 (a–b)). Quantitative EDS analysis (not shown here) indicates that the nanosheets are composed of Bi, Sb and Te elements and the atomic ratio of Bi:Sb:Te is 0.47:1.48:3, which is very close to the nominal composition of Bi$_{0.5}$Sb$_{1.5}$Te$_3$. 

Fig. 5. Typical FESEM images of the products synthesized at 250 °C held for (a) 0, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100 and (g–h) 120 min, respectively.
3.4. Phase evolvement of the Bi$_{0.5}$Sb$_{1.5}$Te$_3$ product with reaction times

In order to comprehensively understand the general development of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ ternary phase, a series of reaction time-dependent experiments were conducted and the phase evolvement was characterized by XRD, shown in Fig. 11. The reaction system was heated to 250 °C with a heating rate of ~3 °C/min and held at 250 °C for various times. The dotted line at 2θ~23.03° indicates the superposition of the Te diffraction peak and Bi$_{0.5}$Sb$_{1.5}$Te$_3$ uncertain one, which can be found in the standard diffraction card (JCPDS card 49-1713) corresponding to rhombohedral Bi$_{0.5}$Sb$_{1.5}$Te$_3$. Another dotted line marked at 2θ~38.2° is used to distinguish the two neighbor peaks corresponding to (1010) plane of Bi$_{0.5}$Sb$_{1.5}$Te$_3$ at 2θ~38.16° and (102) plane of Te at 2θ~38.26°.

At the initial stages (held for 0 and 1 h), Te element phase appeared, like the case of Sb$_2$Te$_3$ formation process as explained above. As the reaction time prolonged to 2–12 h, targeted phase Bi$_{0.5}$Sb$_{1.5}$Te$_3$ appeared accompanied with elemental Te. Besides, intermediate phase hexagonal Sb$_2$Te$_3$ (JCPDS card 72-2183) was detected from the products held for 6–12 h, evidenced by the (018) plane at 2θ~38.8°. The
intermediate phase is a key hint to understand the development of Bi$_{0.5}$Sb$_{1.5}$Te$_3$. Since no signal ascribed to Sb$_2$Te$_3$ or Bi$_2$Te$_3$ was detected in the whole phase evolvement, it is reasonable to deduce that Bi$_{0.5}$Sb$_{1.5}$Te$_3$ has been directly formed by Bi/Sb and Te precursors under the nucleophilic attack of hydrazine hydrate. However, the appearance of Sb$_2$Te$_2$ in XRD patterns gives us a clue for the ternary alloy formation: The disproportionation reaction of Te in basic medium and [Sb$_x$Te$_y$]$_n$ groups self-sustained for an anisotropic assembly may still be deemed as the main route, during which disassociating Bi$^{3+}$ ions combined with [Sb$_x$Te$_y$]$_n$ groups finally to form Bi$_{0.5}$Sb$_{1.5}$Te$_3$.

4. Conclusions

Sb$_2$Te$_3$ and Bi$_{0.5}$Sb$_{1.5}$Te$_3$ nanosheets have been fabricated by a novel gas-induced-reduction (GIR) method. The detailed chemical process has also been studied. Te disproportionation plays a key role and makes the dynamics molecule self-assembly in an anisotropic manner. In addition, selective adsorption mechanism is considered as the important process for the growth of the Sb$_2$Te$_3$ nanosheets. The process of GIR route is proved to be a simple route for manufacturing even ternary Bi–Sb–Te alloys. The established GIR route could be easily extended to other low-dimensional chalcogenide nanostructures and it is convenient to explore related chemical/growth process.

Ethical statement

The authors declare that there is no conflict of interest regarding the publication of this paper.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jmat.2015.10.001.

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